that $CpMo(CO)_3PbPh_3$ reacts with $Ph_3Pb{:}^-$ with $k_2 > 10$ to give $Ph_3PbPbPh_3$ and $CpMo(CO)_3{:}^-$.[8] Since $Ph_3Pb{:}^-$ does not react with Ph_3PbCl to give $Ph_3PbPbPh_3$, the source of the latter in this experiment is not charge–halogen interchange but intermediate formation of the heterodimetallic, mo–pb.

Before summing up these observations it is important to note that it appears that gegenion effects are extremely important in these reactions. For example, if system 17 (mn:$^-$ + sn–Cl) is attempted with Na^+ gegenion, the reported product,[3] in 81% yield, is $(OC)_5MnSnPh_3$. The present study, with Bu_4N^+ gegenion, gives only 30–40%, the remainder being symmetrical products.[5] Attempts to probe gegenion effects have been blocked by the fact that reduction of both the $[CpFe(CO)_2]_2$ and $Ph_3PbPbPh_3$ precursors fails to give stable anion solutions, the latter showing large traces of Pb metal. It is most likely that in the reductions of homodimetallics, a transient dianionic species is produced whose fate is determined by the gegenion. In the present case, with Bu_4N^+, that fate is to give $Ph_3Pb{:}^-$, for example. With Li^+, the fate is perhaps to yield PhLi and Ph_2Pb, the latter redistributing rapidly. In any case, the current observations hold for only the gegenion employed, Bu_4N^+.

In summary then it appears that interactions of m:$^-$ and m–x can lead to at least five possible results, as indicated in eq 2–4. Considerable care must be observed in choosing a reaction to synthesize a metal–metal bond. It is hoped that this work will aid the synthetic chemist choose such a path with logic and certainty.

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Organometallic Electrochemistry. IX.[1] Redistribution Reactions in Homo- and Heterodimetallic Compounds

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Abstract: Approximately 50 redistribution reactions of the type $m{:}^- + m'\text{–}m'' \leftrightarrows m\text{–}m' + m''{:}^-$ have been studied, involving anions derived from the transition and main group elements acting on metal–metal bonds of similar constitution. For $(\pi\text{-}C_5H_5)Fe(CO)_2{:}^-$, $Ph_3Sn{:}^-$, and $Ph_3Pb{:}^-$, the reactions are extremely rapid, with $k_2 > 10\ M^{-1}\ sec^{-1}$ and $K > 100$. The anion extruded from the heterodimetallic compound is always the least nucleophilic (most stable anion). The data have much practical advantage, in that they can aid in predicting, along with facts from previous papers in this series,[1] the proper approach to be used in the synthesis of polymetallic compounds.

Previous papers in this series reported interactions of transition and main group derived anions, m:$^-$, with analogous halides m–x. The discovery of a redistributon reaction of the following type was encountered.

$$m{:}^- + m\text{–}m' \longrightarrow m\text{–}m + m'{:}^- \quad (1)$$

The purpose of this paper is to present the scope of this reaction and discuss the conclusions which may be drawn from Chart I, where the available data are presented. This redistribution reaction, along with the conclusions reached in paper VIII of this series, sets strict boundary conditions on the proper route to heterodimetallic compounds, and thence to polymetallic compounds.

Experimental Section

The basic equipment has been previously described. The necessary compounds and their identification criteria were available from the work described earlier.[1]

In the present study, a homodimetallic compound was dissolved in dry dimethoxyethane containing 0.1 M Bu_4NClO_4. The solution, $2 \times 10^{-3}\ M$ in homodimetallic compound, under argon, was placed in the cathode compartment of an H cell. The anode compartment contained supporting electrolyte and a large Hg pool. The cathode compartment was inletted by standard taper joints to accommodate a reference electrode ($10^{-3}\ M$ Ag^+ Ag), a degassing tube, and a dropping mercury electrode. A polarogram (three-electrode geometry) was taken immediately, using the dme, reference electrode, and Hg pool in the anode compartment. A Metrohm Polarecord, modified to accept a Sargent IR compensator, was used. The connections were then made for controlled-potential electrolysis to two Kepco CK 60-0.5 power supplies wired in master–slave configuration and boot-strapped for high-input impedence. A Heath voltage reference source was used to offset the summing point of the master unit, thus setting the controlled potential, $E_{ref} - E_{test}$, for electrolysis at the large mercury pool in the cathode compartment. Current passed during the electrolysis was monitored by a small dropping resistor in series with the working electrodes, the IR drop being fed into a Yellowsprings instrument recorder. After the current had fallen to the residual level, a polarogram was made to assure that all the parent homodimetallic had been consumed. Then a degassed solution of the desired substrate (to give a $2 \times 10^{-3}\ M$ solution) was injected rapidly, and a polarogram was taken immediately. From the potentials available[1] it was an easy matter to make the assignments shown in Chart I for the resulting products.

Results and Discussion

Chart I presents the products(s) obtained from the interaction of $(\pi\text{-}C_5H_5)Fe(CO)_2{:}^-$, $Ph_3Sn{:}^-$, $Ph_3Pb{:}^-$,

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[1] For previous papers in this series, see R. E. Dessy, *et al.*, *J. Am. Chem. Soc.*, **88**, 453, 460, 467, 471, 5112, 5117, 5121, 5124 (1966).

Chart I

$m:^-$ $-E_{1/2}^{ox}$ m-m $-E_{1/2}^{redn}$	$CpFe(CO)_2:^-$ 1.60	$Ph_3Sn:^-$ 0.95v	$Ph_3Pb:^-$ 0.90	$(OC)_5Mn:^-$ 0.55	$CpMo(CO)_3:^-$ 0.55
fe-fe 2.2	1	7 sn-fe	9 N.R.	11 N.R.	13 N.R.
sn-sn 2.9	6 fe-sn.	2	15 N.R.	17 N.R.	19 N.R.
pb-pb 2.0	8 fe-pb	14 sn-sn	3	21 N.R.	23 N.R.
mn-mn 1.7	10 fe-fe	16 sn-sn	20 ?	4	25 N.R.
mo-mo 1.4	12 fe-fe[b]	18 sn-sn	22 pb-pb	24 N.R.	5
fe-sn 2.6	26 N.R.[a]	31 N.R.	36 N.R.	41 N.R.	
fe-pb 2.1	27 N.R.[a]	32 sn-fe	37 N.R.[a]	42 N.R.	
fe-mo 1.4	28 fe-fe	33 sn-sn + fe-sn	38 pb-fe	43 N.R.	
sn-mo 2.4	29 fe-sn	34 sn-sn	39 ?	44 N.R.[b]	
pb-mo 2.2	30 fe-pb	35 sn-sn	40 pb-pb	45 N.R.	

$(OC)_5Mn:^-$, and $(\pi\text{-}C_5H_5)Mo(CO)_3:^-$ with the homodimetallic species $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$, $Ph_3SnSnPh_3$, $Ph_3PbPbPh_3$, $(OC)_5MnMn(CO)_5$, and $[(\pi\text{-}C_5H_5)Mo(CO)_3]_2$, in addition to the heterodimetallic species fe–sn, fe–pb, fe–mo, sn–mo, and pb–mo.[2] $(\pi\text{-}C_5H_5)Mo(CO)_3:^-$ was not included in the latter study because of its similarity to $(OC)_5Mn:^-$ in nucleophilicity and the lack of reactivity of the latter in all of the systems studied.

In analyzing the results presented in Chart I, it is important to remember that the anions are listed according to their oxidation potential at a Pt electrode, a parameter associated with their nucleophilicity.[3]

Systems 1–5, which involve identity exchanges of the type $m:^- + m\text{–}m \rightleftarrows$, cannot be examined except by radiochemical means; this project will be undertaken shortly.

Systems 6 and 7 (fe:$^-$ + sn–sn, sn:$^-$ + fe–fe) both result in the production of $(\pi\text{-}C_5H_5)Fe(CO)_2SnPh_3$, and $Ph_3Sn:^-$ and $(\pi\text{-}C_5H_5)Fe(CO)_2:^-$, respectively. At the millimolar concentrations employed, and with the time at first analysis being approximately 1 min, the rate constant for redistribution, k_{rd}, must be greater than 10 M^{-1} sec^{-1}. In both cases no sign of the homodimetallic parent was present. Algebraic summation of the two commutations

$$\begin{array}{l} fe:^- + sn\text{–}sn \longrightarrow sn\text{–}fe + sn:^- \\ \underline{sn:^- + fe\text{–}fe \longrightarrow sn\text{–}fe + fe:^-} \\ sn\text{–}sn + fe\text{–}fe \longrightarrow 2sn\text{–}fe \\ K \gg 100 \end{array} \tag{2}$$

suggests that, since solvation effects should not be large and entropy changes small, the strength of a sn–fe bond is greater than the average of the strengths of a fe–fe bond and a sn–sn bond. The oxidation potentials for the two anions would not have predicted both reactions, but it has already been pointed out that the linear correlation observed between oxidation potentials for such anions and nucleophilicity fails for $Ph_3Sn:^-$.

System 8 (fe:$^-$ + pb–pb) gives $(\pi\text{-}C_5H_5)Fe(CO)_2PbPh_3$, while system 9 (pb:$^-$ + fe–fe) shows no reactions over the 5-min standard waiting period. This noncommutation is in agreement with the nucleophilicities of the respective anions.

Both systems 10 (fe:$^-$ + mn–mn) and 12 (fe:$^-$ + mo–mo) yield the homodimetallic species $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$ and the corresponding anions of manganese and molybdenum carbonyls. The commutation experiments (systems 11 and 13) do not, of course, lead to reaction.

At this point it is pertinent to evaluate some of the systems shown in Chart I, in which the reactions of various anions with heterodimetallic species are considered.

Systems 26 and 31 (fe:$^-$ + fe–sn and sn:$^-$ + fe–sn) indicate that there is, as would be predicted, no observable ligand-exchange process occurring, although, of course, it is possible that a fairly rapid fe–fe or sn–sn exchange, respectively, was present. Coupled with the data on system 29 (fe:$^-$ + sn–mo) and system 32 (sn:$^-$ + fe–pb) in which only $(\pi\text{-}C_5H_5)Fe(CO)_2SnPh_3$ is produced, and systems 30 (fe:$^-$ + pb–mo) and 38 (pb:$^-$ + fe–mo) in which only $(\pi\text{-}C_5H_5)Fe(CO)_2PbPh_3$ is produced, the conclusion is that the processes being observed in Chart I are

$$\begin{array}{l} m:^- + m'\text{–}m' \longrightarrow m\text{–}m' + m': \\ m\text{–}m' + m:^- \longrightarrow m\text{–}m + m':^- \end{array} \tag{3}$$

Systems 26 and 27 indicate that $(\pi\text{-}C_5H_5)Fe(CO)_2:^-$ should not react with the intermediate $(\pi\text{-}C_5H_5)Fe(CO)_2\text{–}m$ (m = $SnPh_3$, $PbPh_3$) to yield homodimetallics, but system 28 definitely shows that an intermediate $(\pi\text{-}C_5H_5)Fe(CO)_2Mo(CO)_3(C_5H_5)$ species would react with $(\pi\text{-}C_5H_5)Fe(CO)_2:^-$ to yield the iron homodimetallic. System 12 (fe: + mo–mo) shows that indeed iron dimer is the product.

Whether the reaction stops at heterodimetallic or proceeds to a homodimetallic compound by another redistribution step apparently depends upon the exact nature of the system.

The three pairs of experiments illustrated by systems 14, 15 (sn, pb), 16, 17 (sn, mn), and 18, 19 (sn, mo) show that

$$\begin{array}{c} Ph_3Sn:^- + m\text{–}m \longrightarrow Ph_3SnSnPh_3 + 2m:^- \\ m = pb, mn, mo \end{array} \tag{4}$$

System 34 (sn:$^-$ + sn–mo) agrees that an intermediate $Ph_3Sn\text{–}Mo(CO)_3(\pi\text{-}C_5H_5)$ compound would react with

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[2] m represents a metal, M, and one valence position. The other ligands are as indicated in the parent homodimetallics listed previously in this sentence.

[3] R. E. Dessy, *et al.*, *J. Am. Chem. Soc.*, 88, 5117, 5121 (1966).

$Ph_3Sn:^-$ to give $Ph_3SnSnPh_3$. Unreported in the table is the system $Ph_3Sn{-}Mn(CO)_5 + Ph_3Sn:^-$ which, as predicted, yields $Ph_3SnSnPh_3$. Systems 20 lead to solutions whose polarographic record is impossible to decipher. Compounds, in low concentration, are present that show half-wave potentials in regions that do not correspond to any predictable product. System 21, as is true of all $(OC)_5Mn:^- +$ m–m systems, shows no reaction.

System 22 (pb:⁻ + mo–mo) gives $Ph_3PbPbPh_3$, in agreement with the finding from system 40 that $Ph_3PbMo(CO)_3(\pi\text{-}C_5H_5) + Ph_3Pb:^- \rightarrow Ph_3PbPbPh_3 + (\pi\text{-}C_5H_5)Mo(CO)_3:^-$. The commutation experiment 23 must of course lead to no reaction.

Systems 24–25, as might be expected of the weakly nucleophilic $(OC)_5Mn:^-$ and $(\pi\text{-}C_5H_5)Mo(CO)_3:^-$, do not show evidence of reaction between these anions and the homodimetallics of lead, manganese, or molybdenum.

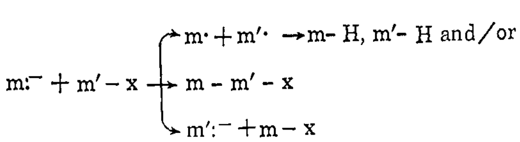
The remaining systems in Chart I were explored in the hopes that some concept of the driving force for the reaction could be found. The key systems are shown in eq 5. In each case, the anion expelled is the least nucleophilic of the two possible anions derivable from the heterodimetallic. In equilibria of the type shown by eq 1, the relative free energies of the two anions involved would be of importance in determining the equilibrium position. This would certainly involve solvation factors. Solvation of the two dimetallic species would be negligible, and their relative enthalpies (bond strength differences) would be of most importance in contributing to free-energy differences. It is hoped that further redistribution studies will lead to equilibria that involve finite constants, and, by canceling out anion effects in paired redistribution studies, a series of bond strengths for metal-metal compounds might be obtained.

$$
\begin{array}{lll}
\text{System} & \text{Components} & \qquad\textbf{Products} \\
28 & \text{fe:}^- + \text{fe–mo} & \longrightarrow \text{fe–fe} + \text{mo:}^- \\
29 & \text{fe:}^- + \text{sn–mo} & \longrightarrow \text{fe–sn} + \text{mo:}^- \\
30 & \text{fe:}^- + \text{sn–mo} & \longrightarrow \text{fe–sn} + \text{mo:}^- \\
 & \text{fe:}^- + \text{pb–mo} & \longrightarrow \text{fe–pb} + \text{mo:}^- \\
32 & \text{sn:}^- + \text{fe–pb} & \longrightarrow \text{fe–sn} + \text{pb:}^- \\
34 & \text{sn:}^- + \text{sn–mo} & \longrightarrow \text{sn–sn} + \text{mo:}^- \\
35 & 2\text{sn:}^- + \text{pb–mo} & \longrightarrow \text{sn–sn} + \text{mo:}^- + \text{pb:}^- \\
38 & \text{pb:}^- + \text{fe–mo} & \longrightarrow \text{pb–fe} + \text{mo:}^- \\
40 & \text{pb:}^- + \text{pb–mo} & \longrightarrow \text{pb–pb} + \text{mo:}^- \\
.. & \text{pb:}^- + \text{pb–mn} & \longrightarrow \text{unidentifiable products} \\
.. & \text{sn:}^- + \text{sn–mn} & \longrightarrow \text{sn–sn} + \text{mn:}^-
\end{array}
\qquad (5)
$$

One possible flaw in this is that the desired systems may not always behave as simply as this picture suggests. For example system 33, according to the developed concepts, should give only $(\pi\text{-}C_5H_5)Fe(CO)_2SnPh_3$, but $Ph_3SnSnPh_3$ is also observed. This appears to be due to a moderate instability of the fe–mo substrate in the system, electron transfer from $Ph_3Sn:^-$ into the decomposition products being the source of the hexaphenylditin. This does not affect the results in systems 28 or 38, since in the former both redistribution and electron transfer would lead to the iron dimer, while $Ph_3Pb:^-$ is a poor electron-transfer source. In addition, some substrates, particularly $(OC)_5Mn{-}m$, seem to undergo displacement of a nonmetallic species when treated with an anion (*cf.* systems 20 and 39 and eq 5).

The remaining systems in Chart I (37 and 41–45) also gave no reaction during the standard 5-min test period because of the poor nucleophilicity of the anion. This, too, would impede a general survey.

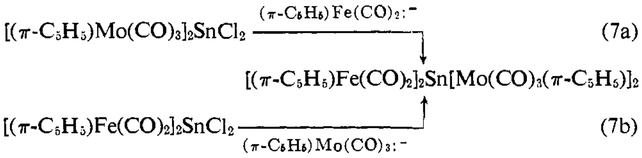
At the moment, the important conclusion to be reached from this set of commutation experiments is that another factor must be added to the hazards involved in forming a m–m′ linkage from the reaction m:⁻ + m′–x. Earlier papers[3] have shown that the rate differences observed in commutation experiments m:⁻ + m–x *vs.* m:⁻ + m–x could easily reach 10^6, urging use of the commutation experiment containing the strongest nucleophile. On the other hand, it has also been shown that the following processes are possible, in addition to the S_N attack leading to establishment of a metal–metal bond



$$
\text{m:}^- + \text{m}'-\text{x} \rightarrow
\begin{cases}
\text{m}\cdot + \text{m}'\cdot \rightarrow \text{m–H, m}'\text{–H and/or } \begin{matrix}\text{m–m}\\ \text{m–m}'\\ \text{m}'\text{–m}'\end{matrix} \\
\text{m – m}' \text{ – x} \\
\text{m}':^- + \text{m} - \text{x}
\end{cases}
\qquad (6)
$$

The present data warn against (a) using the strongest nucleophile and (b) using normal addition (in contrast to reverse addition, *i.e.*, anion to halide where anion is always in a deficiency), since redistribution processes subsequent to the formation of the heterodimetallic may defeat the synthesis, m–m′ + m:⁻ → m–m + m′:⁻. It is suggested that many of the reports in the literature claiming homodimetallic products from such synthetic pathways have involved this factor.

An example of the application of these data would be found in the synthesis of the polymetallic compound



$$
\begin{array}{l}
[(\pi\text{-}C_5H_5)Mo(CO)_3]_2SnCl_2 \xrightarrow{(\pi\text{-}C_5H_5)Fe(CO)_2:^-} \qquad (7a) \\
\qquad [(\pi\text{-}C_5H_5)Fe(CO)_2]_2Sn[Mo(CO)_3(\pi\text{-}C_5H_5)]_2 \\
[(\pi\text{-}C_5H_5)Fe(CO)_2]_2SnCl_2 \xrightarrow[(\pi\text{-}C_5H_5)Mo(CO)_3:^-]{} \qquad (7b)
\end{array}
$$

The lower route has been successfully pursued by Dighe and Orchin.[4] The upper route, on the basis of the present findings, would be an unfavorable one, probably leading to the fe_4Sn compound. With these guide lines established a systematic approach to polymetallic syntheses is being made.

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(4) S. V. Dighe and M. Orchin, *J. Am. Chem. Soc.*, 87, 1146 (1965).